

## COMPOSITIONS AND METHODS FOR WATER SHUT-OFF IN SUBTERRANEAN WELLS

### Cross-Reference to Related Application

**[0001]** This application claims the benefit of U.S. Provisional Patent Application No. 60/403,780 filed August 15, 2002.

### Field of the Invention

**[0002]** The present invention relates to methods and compositions to inhibit or shut-off the flow of water in subterranean formations, and more particularly relates, in one embodiment, to methods of using silica gels to inhibit or shut-off the flow of water in subterranean formations during hydrocarbon recovery operations.

### Background of the Invention

**[0003]** Water production is a major problem in maximizing the hydrocarbon production potential of a subterranean well. Large costs can be incurred from separating and disposing of large amounts of produced water, inhibiting the corrosion of tubulars, replacing tubular equipment downhole, and surface equipment maintenance. Water injection is also a high cost operation. Injecting water into thief zones can decrease the efficiency of the sweep profile and cause oil production to drop. Shutting off unwanted water production and/or maintaining efficient injection profiles are necessary conditions to maintaining a productive field. While there is a wide array of treatments available to solve these problems, they all suffer from a number of difficulties, including, but not necessarily limited to, surface mixing and handling problems, downhole injectivity problems, etc.

**[0004]** Traditional water shut-off technology with chemicals uses sodium silicate solutions employing calcium chloride. Since sodium silicate reacts with calcium chloride instantly to generate gel, the two solutions can be injected in any order and must be separated by a slug of an inert aqueous spacer liquid. U.S. Pat. No. 4,004,639 provides chemicals to achieve water shut-off in producing wells. It uses base fluid sodium silicate solution and gelling agent ammonium

sulfate. Those two solutions are injected and separated by a slug of an inert aqueous spacer liquid. However, these technologies cannot generate uniform gels to plug the porous medium and cannot place the gel deep into the formation. Several staged treatments are also required in the fluids pumping using these techniques.

**[0005]** There is a need to find a chemical system that will simplify the pumping schedule and permit deep penetration into the formation to shut off the water channels.

### Summary of the Invention

**[0006]** Accordingly, it is an object of the present invention to provide a chemical composition for inhibiting or shutting off the flow and/or production of water in and from a subterranean formation.

**[0007]** It is another object of the present invention to provide a chemical composition system and method for use in inhibiting or shutting off the flow and/or production of water in and from a subterranean formation that may be injected at once and that which forms a uniform gel rather than discrete particles.

**[0008]** In carrying out these and other objects of the invention, there is provided, in one form, a method for inhibiting the flow of water in a subterranean formation. The method involves injecting into the subterranean formation a composition that includes a hardener, at least one catalyst, at least one alkali metal silicate, and water. The composition is then permitted to form a silica gel in the subterranean formation for an effective period of time and of a sufficient gel strength to at least inhibit the flow of water in the formation. In one non-limiting embodiment of the invention, the hardener is at least one dialkyl ester of a dicarboxylic acid, the catalyst is an alkali metal hydroxide, which hydrolyzes from the aqueous alkali metal silicate solution, such as aqueous sodium silicate solution.

### Detailed Description of the Invention

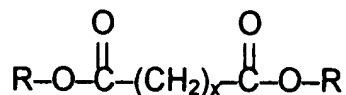
**[0009]** The present invention provides a new silica gel-based system for zone isolation and flow control water shut-off applications. The fluid system comprises sodium silicate solution and a hardener that is added just prior to pumping

to form a single staged treatment. The hardener is from a group of dialkyl esters of dicarboxylic acids including, but not necessarily limited to, dimethyl succinate, dimethyl glutarate, and dimethyl adipate, or mixtures thereof. The inventive fluid system is pumped into the target zone where silica gel is generated *in situ* uniformly. Since silica gel formation occurs *in situ*, better control on the placement of the treatment is achieved and deeper penetration of the shut-off fluid is accomplished with all of the effective permeability of the target zone receiving an effective flow control agent.

**[0010]** A series of laboratory tests have shown that the system can successfully shut off the water production zones in various reservoir conditions from about 70°F to about 300°F. It is expected that the method and compositions of the invention can be effectively used in a broader temperature range between about 50°F to about 350°F. The system has very low viscosity before gelling, which means easy pumping, and has a wide range of gelling times and strengths depending on the type and amount of additives used just prior to use. Without wishing to be limited to any particular parameter range, it is expected that in one embodiment of the invention, the gel strength of the gels formed will range from about 500 to about 15,000 cP, preferably from about 1000 to about 10,000 cP. The single stage treatment may be pumped into targeted formations to provide permanent lost circulation control. The fluid system can also be applied to fix pin-hole casing leaks.

**[0011]** It will be appreciated that although the methods and compositions of this invention have been spoken of as being able to completely shut off water flow in subterranean formations, that the inventive methods and compositions are considered successful even if less than complete shut-off is accomplished. Inhibition, reduction, diminishing, decreasing, and lessening of the water flow through the use of gels of this invention are all considered successful, as are the complete shut-off, prevention, cessation, stoppage, end and termination of water flow, that is, complete control of the water flow.

**[0012]** As noted, the hardener used in the composition is at least one dialkyl ester of a dicarboxylic acid. The hardener may have the formula:



where R is independently selected from straight or branched alkyl groups of 1 to 4 carbon atoms and where x ranges from 1 to 6 carbon atoms. Stated another way, the at least one dialkyl ester of a dicarboxylic acid has alkyl groups independently selected from straight or branched alkyl groups of 1 to 4 carbon atoms, and where the dicarboxylic acid used to make the ester has from 1 to 8 carbon atoms. In a non-limiting, preferred embodiment of the invention, the at least one dialkyl ester of a dicarboxylic acid includes, but is not necessarily limited to, dimethyl succinate, dimethyl glutarate, dimethyl adipate, and mixtures thereof.

**[0013]** The catalyst of the inventive composition includes, but is not necessarily limited to, alkali metal hydroxide, for instance, sodium hydroxide, potassium hydroxide, and mixtures thereof, and tertiary alkanol amines.

**[0014]** The alkali metal silicate of the inventive composition may include, but is not necessarily limited to, sodium silicate, potassium silicate, and sodium/-potassium silicate mixtures, in one non-limiting embodiment of the invention.

**[0015]** Although the proportional makeup of the inventive composition may vary widely depending upon a number of factors including, but not necessarily limited to, the nature of the formation, the formation conditions (e.g. temperature, pressure, permeability, etc.), the particular composition components, the injection method, the interaction of these various factors, and the like, in one non-limiting embodiment of the invention, the composition comprises from about 0.5 to about 2.5 v/v% hardener, from about 0.01 to about 5.0 wt% catalyst, from about 0.025 to about 10.00 v/v% alkali metal silicate, based on the total composition. In a preferred, non-limiting embodiment of the invention, the composition comprises from about 0.5 to about 1.5 v/v% hardener, from about 0.05 to about 2.50 wt% catalyst, from about 1.00 to about 2.50 v/v% alkali metal silicate, based on the total composition. Water may form the balance of the composition, but other components may be added, including, but not necessarily limited to, quaternary amines, alkoxylated quaternary amines, and alkoxylated phenols and alcohols

(typically ethoxylated phenols and alcohols). These additives can help reduce clay swelling and/or reduce surface tension for more even distribution of the components.

**[0016]** In one non-limiting embodiment of the invention, the present method is practiced in the absence of a gas, and/or in the absence of a non-esterified organic acid.

**[0017]** The invention will be further illustrated with respect to certain experiments, but these examples are not intended to limit the invention, but only to further describe it in certain specific, non-limiting embodiments.

Table 1  
Gelling Time for Different Fluid Formulae at Different Temperatures

<u>Ex.</u>	<u>Temperature (°F)</u>	<u>Formula (%v/v)</u>	<u>Gelling Time (min)</u>	<u>Gel*** Strength (cP)</u>
1	104	2.50%SS* + 2.50%DBE**	90	1800
2	150	2.50%SS + 1.50%DBE	70	650
3	150	2.50%SS + 1.20%DBE	150	650
4	200	2.00%SS + 1.25%DBE	55	500
5	212	1.50%SS + 1.75%DBE	90	250
6	250	2.00%SS + 0.50%DBE	220	1100
7	302	1.00%SS + 0.75%DBE	210	700

\*SS – 37.5% wt. (1.40 g/cm<sup>3</sup>) of sodium silicate solution.

\*\* DBE – Mixture of Dimethyl Glutarate, Dimethyl Adipate, and Dimethyl Succinate.

\*\*\* Before gelling, the viscosities of the solutions are less than 5 cP.

**[0018]** The results of Examples 1-7 of Table 1 demonstrate that different fluid formulae can provide acceptable gel strengths within suitable gelling time frames at a variety of temperatures.

Table 2  
Sand Pack Plugging Tests

<u>Ex.</u>	<u>Sand pack size (Diameter (in.) x Length (in.))</u>	<u>Tempera- ture (°F)</u>	<u>Formula (%v/v)</u>	<u>Permeability before fluid displacement (md)</u>	<u>Permeability After fluid displacement (md)</u>
8	2.5 × 6.0	250	2.00%SS + 0.63%DBE	1710	0.73
9	2.5 × 6.0	300	1.50%SS + 0.50%DBE	2100	0.89

**[0019]** The results of Examples 8-9 of Table 2 demonstrate that different fluid formulae can effectively reduce the permeability of a sand pack at different temperatures.

**[0020]** In the foregoing specification, the invention has been described with reference to specific embodiments thereof, and has been demonstrated as effective in providing a method of inhibiting and/or shutting off water flow in subterranean formations. However, it will be evident that various modifications and changes can be made to the inventive compositions and methods without departing from the broader spirit or scope of the invention as set forth in the appended claims. Accordingly, the specification is to be regarded in an illustrative rather than a restrictive sense. For example, specific combinations of hardeners, catalysts, alkali metal silicates and other components falling within the claimed parameters, but not specifically identified or tried in a particular composition or under specific conditions, are anticipated to be within the scope of this invention.